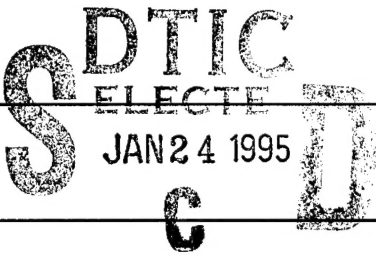# REPORT DOCUMENTATION PAGE

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New mechanism for the desorption of excited atoms by photon bombardment of alkali halide crystals

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We report measurements of photon-stimulated desorption of excited atoms from LiF and NaCl crystal surfaces. Based on these measurements, we propose a new model of photon-initiated, defect-mediated desorption involving exoergic surface reactions between alkali dimers and halogens. This model consists of two steps: (a) reactants are formed at the surface, directly or by the migration to the surface of holes and defects created in the near surface bulk, due to uv photon bombardment, and (b) excited alkali atoms are emitted following a reaction between the alkali and halogen surface species.

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In this letter we present a new model for desorption of excited alkali atoms from alkali halide crystal surfaces following photon bombardment. The mechanisms responsible

for the production of excited alkali atoms by photon-stimulated desorption (PSD) and electron-stimulated desorption (ESD) have been the subjects of much controversy. Two models have been invoked most often to account for the production of the excited atoms. One model involves ion neutralization, and is analogous to the Knotek-Feibelman mechanism for ion desorption.[1,2] According to this mechanism, the interatomic Auger decay of a core hole results in the formation of two valence holes on a single surface anion resulting in ion desorption. Subsequent neutralization of the desorbing ion into an excited state then accounts for the observed excited atom yield. The second model assumes that the excited atoms are produced by secondary-electron excitation of desorbed ground state atoms in the gas phase.[3-6] Recent work[7] shows that valence excitations alone can lead to excited alkali atom desorption; thus core-hole creation, an essential component of the Knotek-Feibelman mechanism, is not always required for the production of excited alkali atoms. Previous work[7-11] also shows that the excited alkali atom yield of PSD decreases markedly with increasing temperature while both the total electron yield and ground state alkali atom yield increase, in contradiction to the second model involving secondary electron excitation. Thus, both models have been found to exhibit deficiencies when applied to PSD.

The new mechanism we propose is based on one or more exoergic surface reactions between alkali dimers (M_2) and halogens (X or X_2). The most direct possible reaction[12-19] is $M_2 + X \rightarrow M^* + MX$.[20] This reaction was first suggested to explain the observation of sodium D-lines when sodium vapor was mixed with chlorine, bromine, or iodine gas.[12] In general, the reaction occurs with most of the possible combinations of alkali vapors and halogen gases. Subsequently this reaction was studied directly by molecular-beam experiments[13-17] and its feasibility was demonstrated by semiempirical theoretical calculations.[18] The gas-phase reaction cross section for producing excited alkali atoms was

2

found by theoretical calculations[19] and by crossed beam studies[13-17] to be very large, $10 - 100$ Å^2. Figure 1, based on the calculations in Struve's paper,[18] depicts a section of the energy surface of collinear Na$_2$Cl. The reaction proceeds through a transition state in which an electron from the sodium dimer shifts to the chlorine atom positioning the excited molecular complex, (Na–Na$^+$Cl$^-$)*, at a point on the potential energy surface corresponding to neutral sodium in a repulsive state. The system may then evolve through this position to form a free sodium atom in its first excited state and an ionically bonded NaCl molecule. The available reaction energy is no greater than 3.50 ± 0.04 eV for Na$_2$+Cl and 3.30 ± 0.13 eV for Li$_2$+F.[21] This limitation rules out the population of those higher excited states that decay in the visible, unless there is a contribution from reagent collision energy. (Polanyi et al.[16] found that, in molecular beam experiments, higher excited states are populated for collision energies in the range 0.2 to 0.5 eV. The first excited state, however, is always populated at least an order of magnitude more than the higher excited states.)

The proposed model depends upon the presence of alkali dimers and halide atoms on the surface. It is well accepted that in PSD or ESD from alkali halide crystals at elevated temperatures the majority desorbing species are ground state halogen atoms and alkali atoms.[22,23] The desorption of these ground state halogen and alkali atoms is thought to be mediated by self-trapped excitons created either on the surface or in the bulk.[24-26] The incident photon or electron creates one or more holes in occupied valence bands in the near surface bulk. Energetic "hot" holes may migrate within a picosecond, some further into the bulk and some to the surface, before coming to rest and forming self-trapped excitons.[23] Self-trapped excitons in the bulk may then decay forming an F-center/H-center pair.[25,26] Subsequent thermally assisted migration of the H-center can produce temperature-

equilibrated halogen at the surface, some of which thermally desorbs leaving excess metal. Nonthermal halogen emission may arise from the decay of surface self-trapped excitons again resulting in excess metal.[27] Depending on the degree of metallization, which in turn depends on the irradiation history and temperature, the accumulated neutralized alkali atoms may then form dimers, trimers, and larger clusters on the surface.[28,29] At some accumulated irradiation dosage, the number of dimers should reach a maximum. Thus during photon or electron bombardment of alkali halide crystals, defect mediated processes create at the surface the necessary reactants for the postulated reaction.

The PSD experiments reported here were performed at the Synchrotron Radiation Center of the University of Wisconsin with the Vanderbilt/SRC 6-meter toroidal-grating monochromator, which provides photons in the energy range of 7 to 180 eV. Excited atoms were detected by monitoring their characteristic optical emission above the surface with a MacPherson 218 monochromator and an EMI S-20 photomultiplier tube. After cleaving, the alkali halide single crystals were exposed to air for less than 30 minutes before the chamber was evacuated. The crystals were then annealed six to eight hours at 350° C.

Shown in figures 2a and 2b are optical spectra of LiF and NaCl crystals under photon bombardment. Sharp peaks superimposed on the continuous bulk luminescence correspond to atomic transitions from the 2p to the 2s state for lithium atoms and the 3p to the 3s state for sodium atoms, respectively. Transitions from higher excited states, such as from the 3p to the 2s state for lithium atoms (323.3 nm) and from the 4p to the 3s state for sodium (330.2 nm) are not seen in our spectra, but will be searched for in future experiments. The absence of the higher states is consistent with the prediction of our surface-reaction model: the reaction energy available is not sufficient to populate higher states provided the reactants on the surface have negligible collision energy.

Figure 3 shows the excited lithium atom yield plotted as a function of irradiation time during 62.2 eV photon bombardment of LiF. The yield was normalized to the photon

flux. The dependence of the yield on the irradiation time, shown in Fig. 3, is consistent with the hypothesis that the yield reflects the instantaneous alkali dimer concentration which in turn depends largely on the degree of metallization of the surface. The nonzero yield at the beginning of the measurement is due to the presence of metal on the surface, even for the annealed samples.[28] Initially there are relatively few alkali dimers on the surface; thus even though the halogen yield is large at this stage, the excited atom yield is small. As the metallization increases, there is an optimum stage where many alkali dimers are present while the halogen atom concentration remains large. At this stage the excited alkali atom yield is at a maximum as indicated by the peak in figure 3. With further irradiation the yield decreases because of a decrease in the concentration of dimers due to the formation of larger clusters, and because the metal clusters block halogen atom desorption.

Figures 4a and 4b are plots of the yields of excited Li atoms from LiF and excited Na atoms from NaCl, respectively, as functions of time, showing the effects of transient halogen dosing during uv photon bombardment. To increase the yields, incident zero-order light transmitted through an aluminum filter was used for both of these measurements. Yields were normalized to photon flux. Chlorine gas was introduced into the chamber for a period of 10 seconds resulting typically in an exposure of 86 Langmuirs and causing large enhancements in the excited atom yield for both samples. These observations are consistent with the hypothesis that the enhancements were due to the increase of the concentration of chlorine atoms on the surface. We postulate that chlorine molecules are dissociated on the surface, providing the required chlorine atoms. Note that the enhancement in Li* yield in the LiF case is due to the action of the externally introduced chlorine atoms in contrast to internally generated fluorine atoms. This is a strong evidence that reactions occurring on the surface, as postulated, lead to the emission of the excited metal atoms.

We postulate that our proposed mechanism is also a contributor to *electron*-stimulated desorption of excited alkali atoms. Other likely contributors include excitation of

5

desorbed ground-state neutral alkalis by primary beam electrons[4,5] and also to some extent by secondary electrons.[3] In support of this postulate, for the case of LiF we have previously measured the temperature-dependent yield of excited lithium atoms during electron bombardment.[9] The yield was found to be appreciable at room temperature (where desorption of thermal ground-state atoms is low) but increased by two orders of magnitude with temperature up to 400° C (where radiation induced desorption of ground state lithium atoms is increased by *four* orders of magnitude).[9] In contrast, the yield from photon-stimulated desorption is also appreciable at room temperature but *decreases* markedly with increasing temperature.[7,8] This indicates that (a) for PSD, there is little contribution from gas-phase excitation by secondary electrons, and (b) for ESD at low temperatures, where gas-phase excitation does not contribute because the desorption yield of ground-state alkalis is low, our proposed mechanism is the principal contributor.

In conclusion, we suggest a new model for the production of excited alkali atoms by PSD. This model is based on experimental measurements of photon-stimulated desorption and the previously known gas-phase chemiluminescent reaction between alkali dimers and halogen atoms. Radiation-induced metallization and halogen atom formation provide the two necessary reactants for the surface reaction. The large enhancement of the excited alkali atom yield due to chlorine dosing, the dependence of the yield on the irradiation time, and the apparent absence of visible emission from other excited electronic states are in strong support of the new model.

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Figure Captions

Figure 1: A schematic representation of a section of the semiempirical energy surface for the collinear $Na_2+Cl \rightarrow Na^*+NaCl$ reaction based on figure 1 of Struve's paper (ref. 18). The vertical axis represents energy, the R_1 axis the distance between the two sodium atoms, and the R_2 axis the distance between a chlorine atom and the nearer sodium atom of the dimer.

Figures 2a and 2b: Optical fluorescence spectra of LiF and NaCl crystals, respectively, due to photon bombardment.

Figure 3: Effect of irradiation time on the yield of excited lithium atoms. The photon energy was 62.2 eV and the yield is normalized to the Ni mesh current.

Figures 4a and 4b: Effect of chlorine gas dosing on the yields of excited alkali atoms from LiF and NaCl crystals, respectively, under zero-order light bombardment. Dosings started at 0th minute and lasted for 10 seconds.
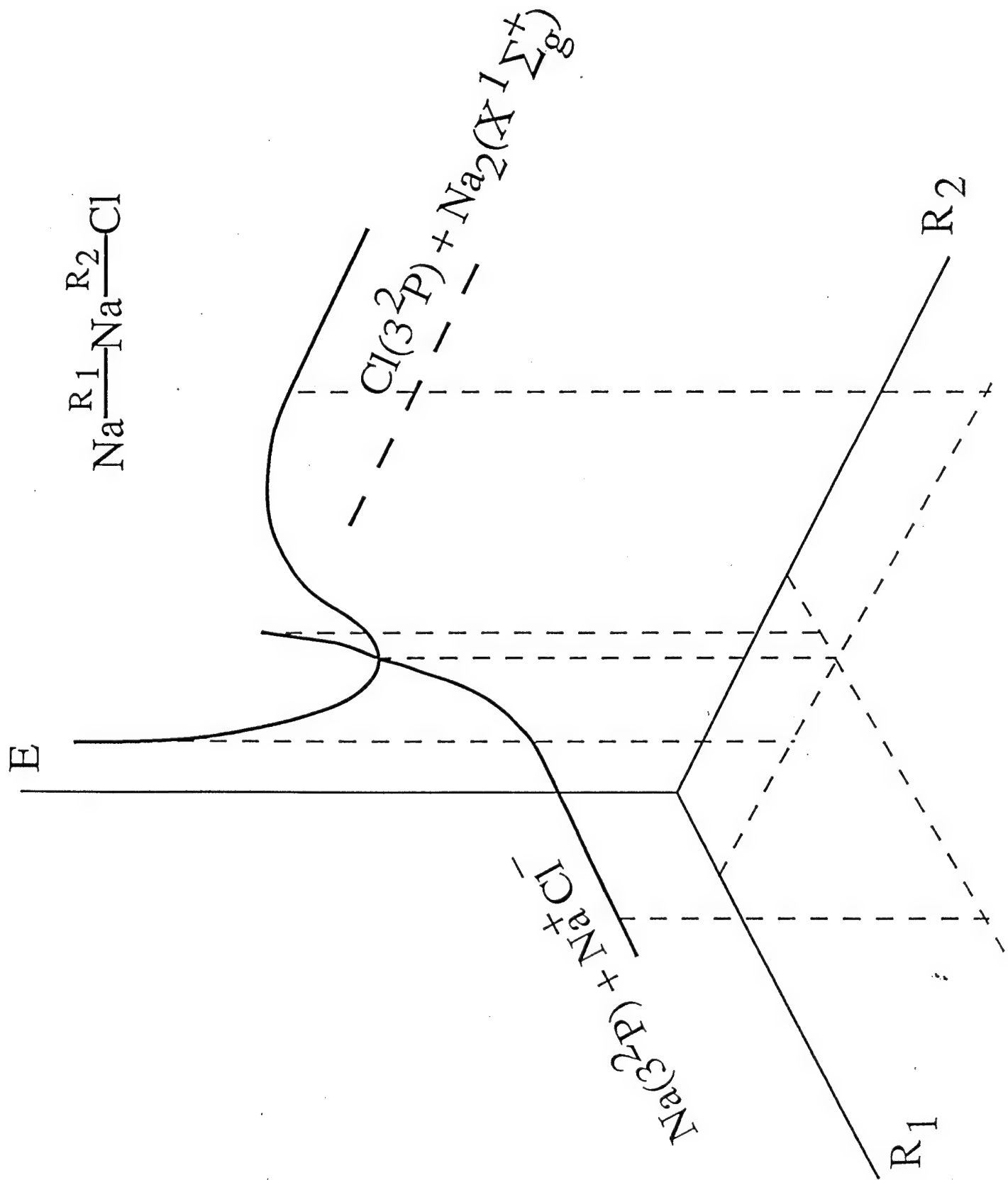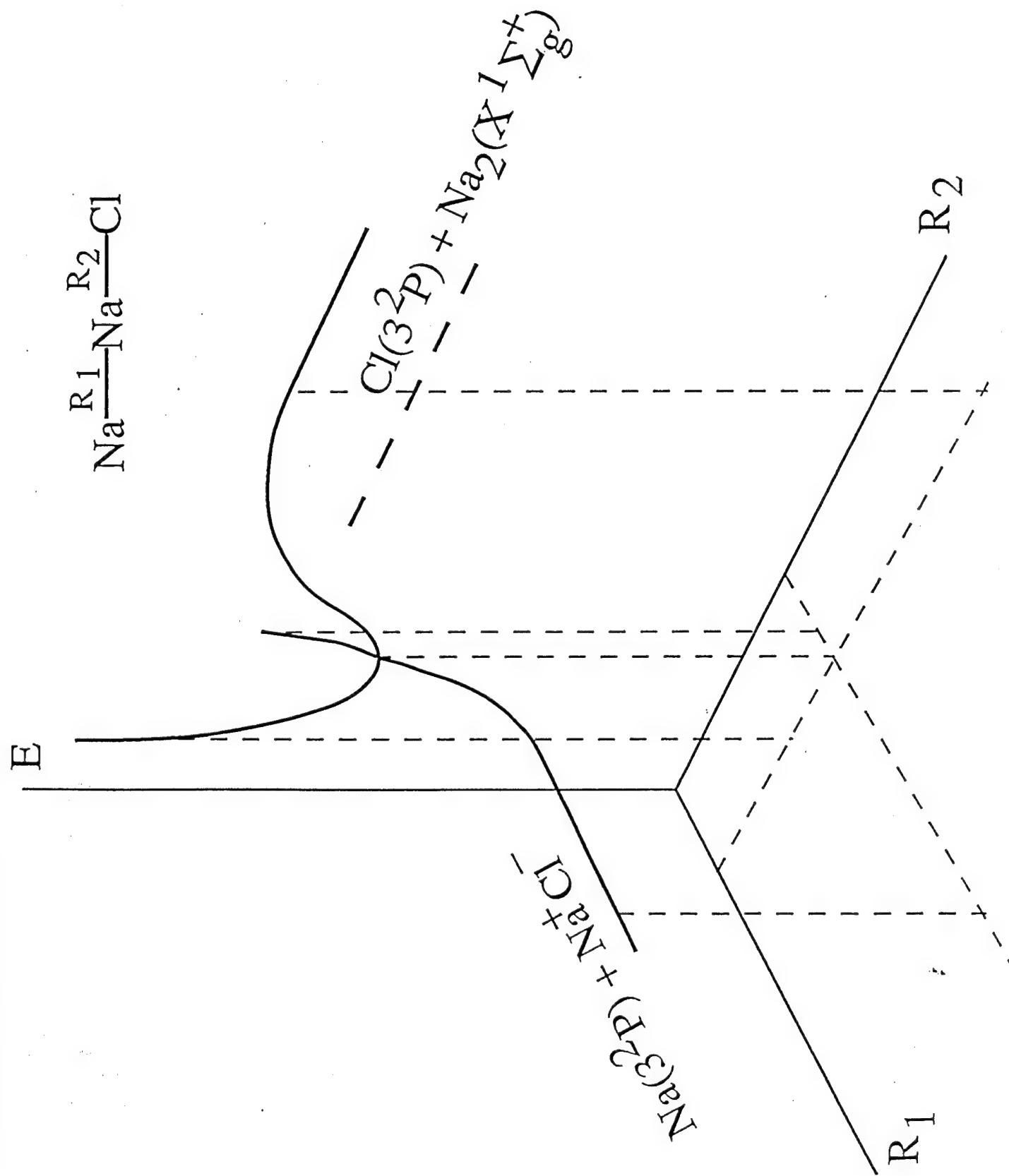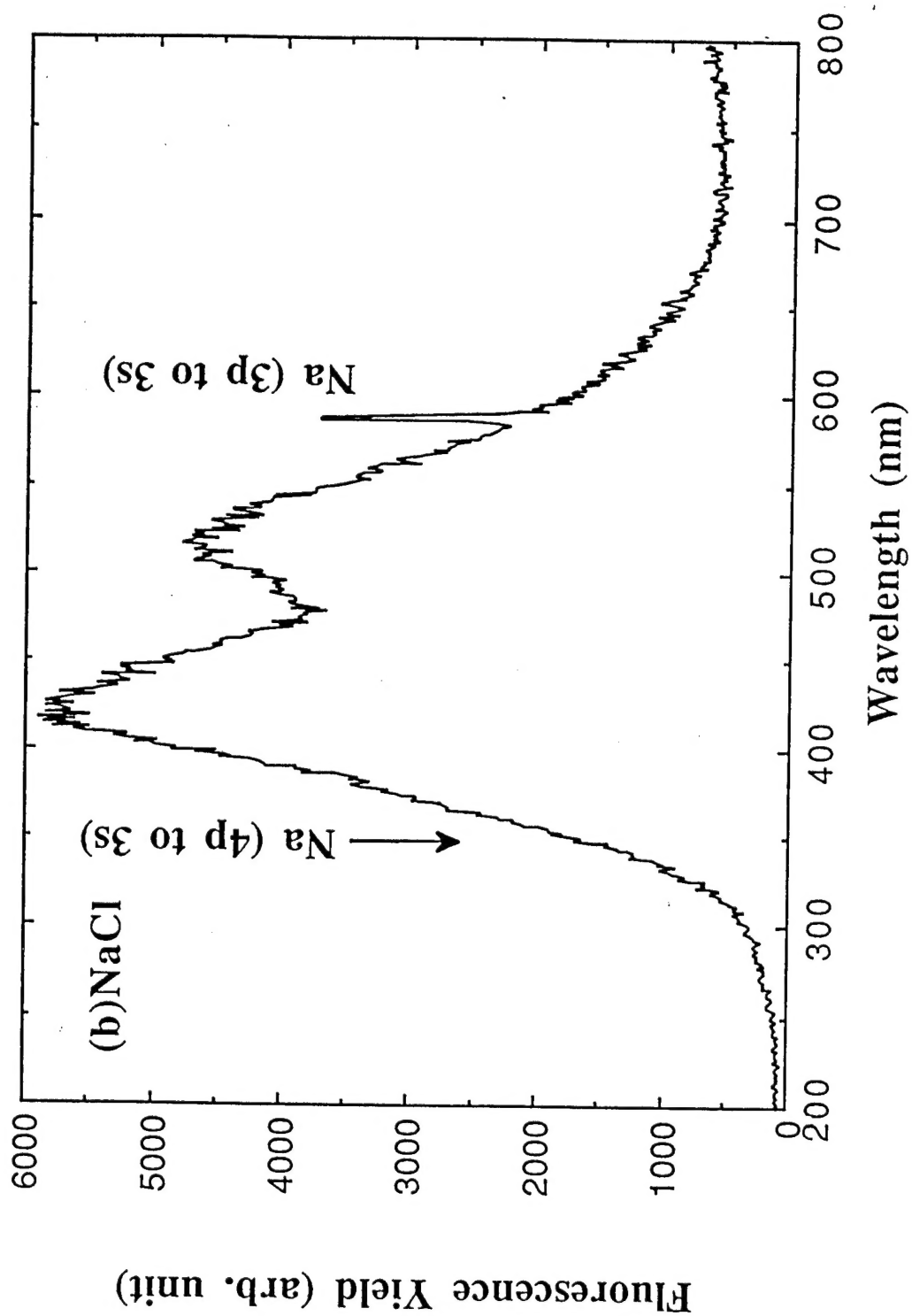
Fig.

Fig.

Fig. 2b

(b)NaCl
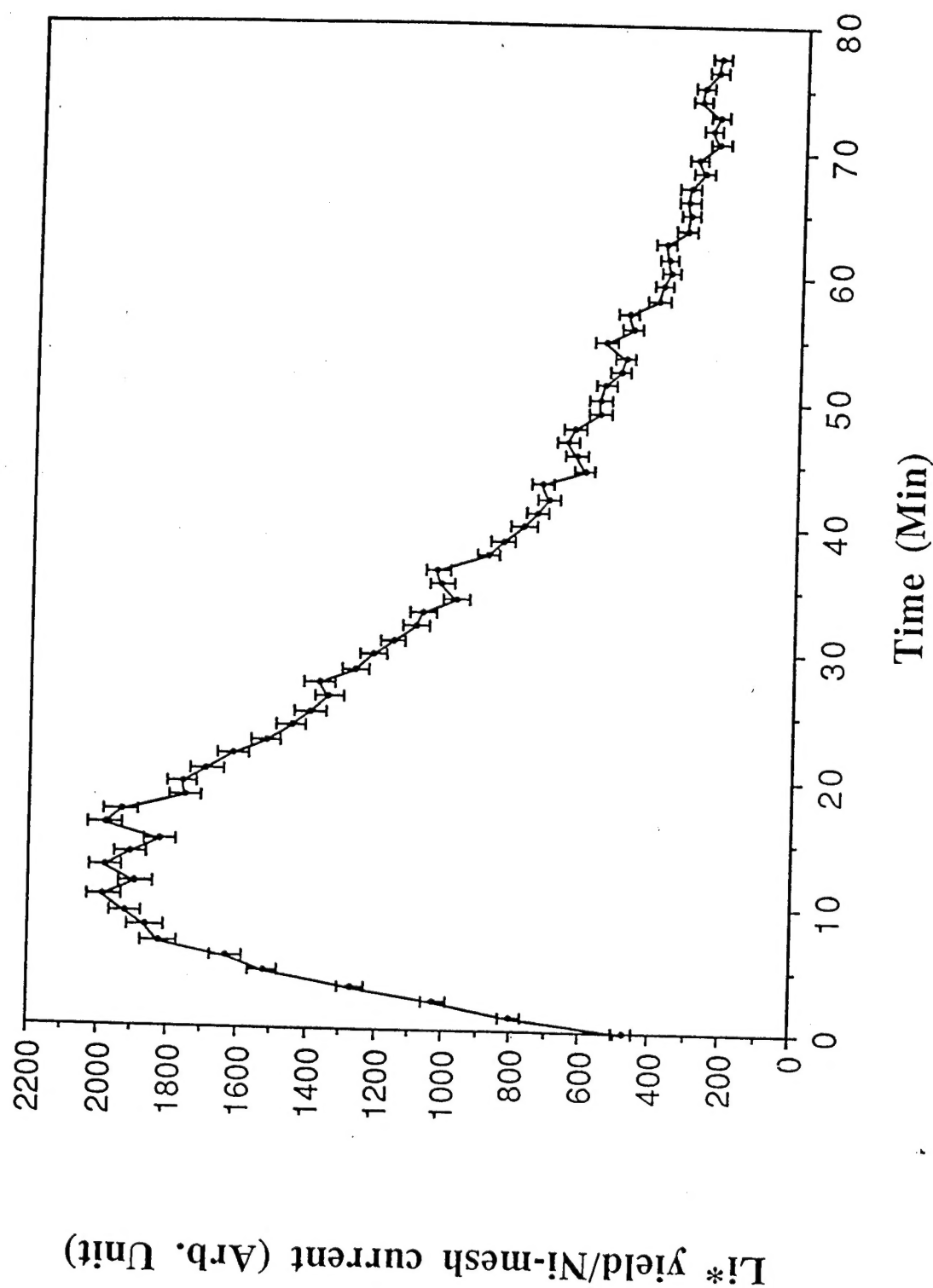
Na (4p to 3s) →

Na (3p to 3s)

Wavelength (nm)

Fluorescence Yield (arb. unit)

Fig 3

Li* yield/Ni-mesh current (Arb. Unit)

Time (Min)

Fig. 4a

(a)

dosing onset →

Li* yield/Ni-mesh current (arb. unit)

Time (min.)

Fig. 4b

(b)

dosing onset →

Time (min.)

Na* yield/Ni-mesh current(arb. unit)